



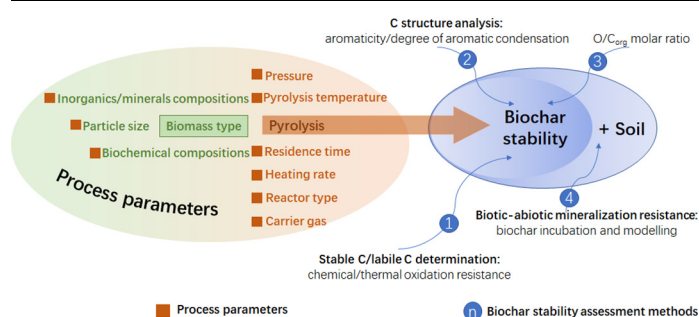
Review

An overview of the effect of pyrolysis process parameters on biochar stability

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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Mineralization
Oxidation stability
Aromaticity
Degree of aromatic condensation
Pyrogenic carbon materials
Charcoal

ABSTRACT

Biochar produced from biomass pyrolysis is becoming a powerful tool for carbon sequestration and greenhouse gas (GHG) emission reduction. Biochar C recalcitrance or biochar stability is the decisive property determining its carbon sequestration potential. The effect of pyrolysis process parameters on biochar stability is becoming a frontier of biochar study. This review discussed comprehensively how and why biomass compositions and physicochemical properties and biomass processing conditions such as pyrolysis temperature and reaction residence time affect the stability of biochar. The review found that relative high temperature (400–700 °C), long reaction residence time, slow heating rate, high pressure, the presence of some minerals and biomass feedstock of high-lignin content with large particle size are preferable to biochar stability. However, challenges exist to mediate the trade-offs between biochar stability and other potential wins. Strategies were then proposed to promote the utilization of biochar as a climate change mitigation tool.

1. Introduction

Pyrolysis, gasification, and hydrothermal carbonization/liquefaction are commonly used high-temperature treatment processes for converting biomass to produce solid, liquid, and gas products such as biochar, bio-oil, and biogas (Huang and Yuan, 2015; Lai et al., 2018;

Leng et al., 2018a, 2018b, 2018c; Li et al., 2018; Wang et al., 2017, 2018). Among these products, biochar has attracted global attention due to its great potential applications in a wide range of areas such as wastewater treatment, soil amendment and remediation, CO₂ capture, climate change mitigation and energy storage (Ahmad et al., 2014; Chen et al., 2015; Leng et al., 2015a, 2015b; Liu et al., 2015; Sohi et al.,

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<https://doi.org/10.1016/j.biortech.2018.09.030>

Received 3 August 2018; Received in revised form 5 September 2018; Accepted 6 September 2018

Available online 07 September 2018

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2010; Tan et al., 2017, 2015, 2016). The use of biochar for climate change mitigation is mainly based on sequestering biochar C from degradation and reducing the soil-derived greenhouse gases (GHGs) emissions (Lehmann et al., 2011, 2008, 2006; Sohi et al., 2010). When biochar is considered as a tool for climate change mitigation, biochar produced from pyrolysis is generally used (EBC, 2012; IBI, 2015; Lehmann et al., 2006).

Biochar, as a carbon sequester, is based on the idea that biochar C can persist in soil for hundreds of years long or longer (Lehmann, 2007a, 2007b; Lehmann et al., 2006). It is much recalcitrant to degradation in soil than its original organic feedstock which degrades within several years. Biochar stability is the decisive factor that determines C degradation or C sequestration potential (Leng et al., 2019). Elemental and chemical compositions, and carbon structures are the main properties closely related to biochar stability (Leng et al., 2019), and different biochar properties lead to varied biochar stability. The differences of these properties are because of pyrolyzing different biomass type under various process conditions. Many studies have been carried out to investigate the effect of these processing parameters including biomass feedstock compositions and properties and pyrolysis conditions on biochar stability (Leng et al., 2019; Weber and Quicker, 2018). For example, lignin content (Windeatt et al., 2014) and mineral content (Han et al., 2018) of biomass, biomass particle size (Manyà et al., 2014b), pyrolysis temperature or heat treatment temperature (HTT) (Han et al., 2018; Harvey et al., 2012; Wiedemeier et al., 2015b), reaction residence time (Conti et al., 2016), heating rate (Chen et al., 2016a), pressure (Manyà et al., 2014b), and pyrolyzer configurations (Jegajeevagan et al., 2016) were reported to have influence on biochar stability.

The present review aims to give comprehensive and detailed up-to-date information on the effect of these process parameters on biochar stability, providing instructions on production of biochar with preferable stability. Challenges and research needs were also discussed to promote utilization of biochar as a climate change mitigation tool.

2. Biochar properties related to biochar stability

2.1. Carbon structures

Carbon structures, i.e., aromaticity and aromatic condensation of biochar are the direct information for assessing the stability of biochar (dominated by aromatic C). The formation of rings of C atoms and their condensation and growth into larger sheets and stacks are the origins of aromatic C. Aromaticity and degree of aromatic condensation are two indices to evaluate the stability of carbon materials (Table 1). High aromaticity and degree of aromatic condensation are indicative of high stability of biochar. The degree of aromatic condensation ($-\Delta\delta$) and nonaromatic C proportion of biochar obtained by nuclear magnetic resonance (NMR) analysis are closely correlated with mean residence time (MRT) ($\text{MRT} = 148 * e^{1.144 * (-\Delta\delta)}$, $R^2 = 0.953$; $\text{MRT} = 1682 * (\text{nonaromatic C content})^{-0.696}$, $R^2 = 0.940$) (Singh et al., 2012a). Sizes

of turbostratic crystallites estimated by X-ray diffraction (XRD) analysis are also positively correlated with aromaticity (Keiluweit et al., 2010; Lehmann and Joseph, 2015). The modern definition of aromaticity (International Union of Pure and Applied Chemistry, IUPAC) is the concept of spatial and electronic structure of cyclic molecular systems displaying the effects of cyclic electron delocalization which provide for their enhanced thermodynamic stability (relative to acyclic structural analogues) and tendency to retain the structural type during chemical transformations. Only π -systems containing 2, 6, 10, 14, or more electrons exhibit the enhanced stability that is associated with aromaticity (Lehmann and Joseph, 2015).

Biochar is a complex matrix which has a range of potential chemical compositions and physical structures, with different degrees of aromatic linked sheet development (graphitic sheets) and incidence of these defect structures (Lehmann and Joseph, 2015). The content of energetically stable aromatic ring structures in biochars is very important as it contributes decisively to both fate and reactivity of biochar in the environment. The degree of aromatic condensation or the extent to which aromatic rings are clustered into larger poly-condensed units becomes the central determinant of biochar functionality and persistence in the environment. Type of feedstock, maximum pyrolysis temperature, and the duration of the heat treatment are three of the most evident factors controlling the aromaticity of biochars.

Non-aromatic structures/function groups can also be important to biochar stability. Clusters of fused aromatic rings are connected, or cross-linked, by non-aromatic structures such as alkyl ($-\text{CH}_n-$) and carbonyl ($-\text{C}(\text{O})-$) side chains. Non-aromatic structures help to form clusters and affect the size of the domain and the stability of biochars.

2.2. Elemental compositions

Elemental compositions are decisive to biochar stability and the mole ratios have been developed as biochar stability proxies (Table 1). Data from CHNO elemental analyses allow to analyze the stoichiometry of biochar by empirical formulae, $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$, the molar quantities displayed by the formulae are then amenable for treatment by traditional organic chemistry concepts (Lehmann and Joseph, 2015). Since N is only a minor element of biochar (Fig. 1), the unsaturation or aromaticity of biochar may be assessed by C, H, and O compositions, that is H/C and/or O/C ratios. The molar ratio of $\text{H}/\text{C}_{\text{org}}$ has been adopted by IBI and lower ratio of $\text{H}/\text{C}_{\text{org}}$ corresponds to greater stability (IBI, 2015). EBC also made requirements on both $\text{H}/\text{C}_{\text{org}}$ and $\text{O}/\text{C}_{\text{org}}$ for indicative of biochar stability (EBC, 2012). Pyrolysis favors dehydration and deoxygenation, and thus promotes the elimination of H and O over C, resulting in the accumulation of C in solid residue biochar. The contents and ratios of these elements are the most important factors influence the stability or carbon sequestration capacity of the biochar. Biochar lability related directly to oxygen content and indirectly to C content (Zimmerman, 2010). Both H/C and O/C ratios are indicative of structures of biochar, and thus provide an intrinsic measurement of the stability of biochar. The H/C and O/C ratios correlate negatively with

Table 1
Relationships between biochar properties and biochar stability.

Properties	Specifications	Relationships with biochar stability
C structure	<ul style="list-style-type: none"> ■ Aromaticity ■ Degree of aromatic condensation 	<ul style="list-style-type: none"> ■ Aromaticity ■ Degree of aromatic condensation ■ Oxidation resistance ■ Biotic-abiotic mineralization resistance in soil
Elemental/chemical compositions	<ul style="list-style-type: none"> ■ Elemental compositions ■ Functionality ■ Content of minerals 	<ul style="list-style-type: none"> ■ $\text{O}/\text{C}_{\text{org}}$, $\text{H}/\text{C}_{\text{org}}$ ■ Aromaticity ■ Oxidation resistance ■ Biotic-abiotic mineralization resistance in soil
Physical and chemical properties	<ul style="list-style-type: none"> ■ Particle size, pore volume, surface area, density, wettability, pH, toxicity, etc. 	<ul style="list-style-type: none"> ■ Oxidation resistance ■ Biotic-abiotic mineralization resistance in soil

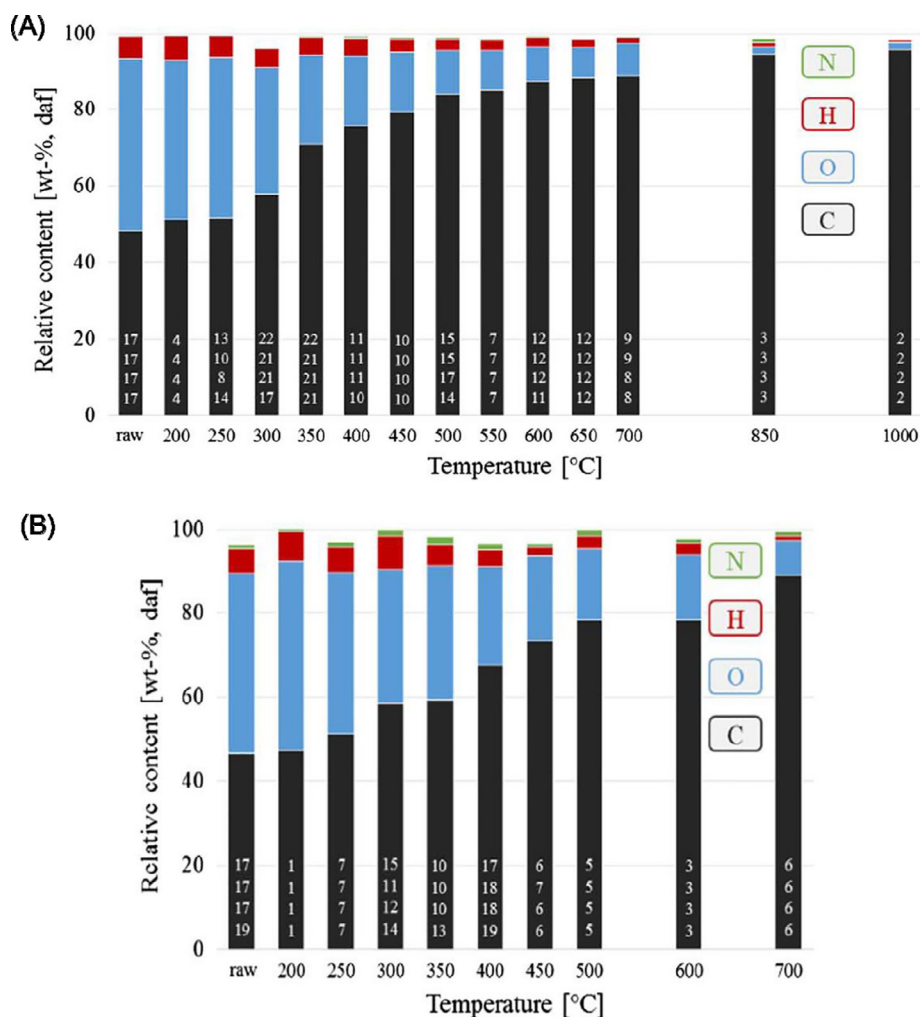


Fig. 1. Elemental compositions of biochar from (A) woody and (B) straw-like biomass (Weber and Quicker, 2018). Numbers given in each column mean the number of elemental composition values used for plotting the graph.

the percentage of aromatic C (aromaticity) in biochar (Manyà et al., 2014b).

Oxygen content plays an important role in biochar surface chemistry behavior because of its close relationship with the number and composition of the substituted functional groups, and these functional groups constitute an important driver for degradation potential. The O/C ratio assigned to materials encompassed by the black C continuum (Fig. 2) shows a systematic increase from 0 for graphite to > 0.6 for materials which cannot be considered to be black C (Spokas, 2010). The position of a material on the black C continuum has major influence on the thermal and chemical stability of this material. However, biochar is not a single chemical entity (Spokas, 2010). With large variability on its compositions, biochar may be treated as part of the black C continuum

in both variable structure and chemical compositions. Spokas (2010) claimed that biochars with an O/C molar ratio of less than 0.2 are typically the most stable, possessing an estimated half-life of more than 1000 years; biochars with an O/C ratio of 0.2–0.6 have intermediate half-lives of 100–1000 years; and, finally biochars with an O/C ratio of greater than 0.6 possess a half-life in the order of < 100 years.

The molar H/C ratio may be used to assess the degree of thermochemical alteration that produces fused aromatic ring structures in the material. Lower H/C means the higher fused aromatic ring structures and the higher stability. It is an index of aromaticity and resistance of char to microbial and chemical degradation (Kuhlbusch, 1995). The molar H/C ratio is a typical indicator for the degree of unsaturation or the amount of C=C double bonds in organic polymers by calculating

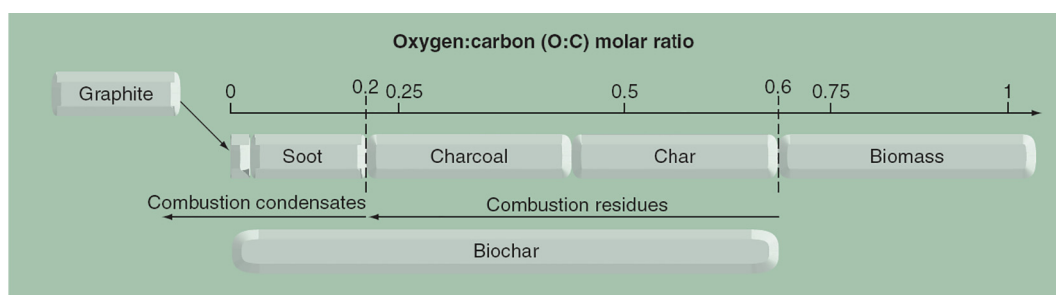


Fig. 2. The spectrum of combustion product (black carbon) continuum. Reprinted from (Spokas, 2010).

Table 2
Methodologies used for biochar stability assessment.

Methodology category	Commonly used biochar stability assessment methodologies
C structure analysis (analysis of aromaticity/degree of aromatic condensation)	<ul style="list-style-type: none"> ■ Analysis of aromaticity by i) instrumental analysis such as solid-state ^{13}C Nuclear magnetic resonance spectroscopy (NMR) (Wiedemeier et al., 2015b), X-ray diffraction (XRD) (Keiluweit et al., 2010), Near-edge X-ray absorption fine structure (NEXAFS) (Wiedemeier et al., 2015a), Mid-infrared spectroscopy (MIR) (Kusumo et al., 2014), X-ray photon spectroscopy (XPS) (Yang et al., 2016), and Fourier transform infrared spectroscopy (FTIR) (Hernandez-Soriano et al., 2016), ii) molecular markers such as benzene polycarboxylic acid (BPCA) (Wiedemeier et al., 2015b) and markers from Pyrolysis-GC-MS (Conti et al., 2016, 2014) and HydroPyrolysis-GC-MS (Rombolà et al., 2016), iii) He pycnometry (Wiedemeier et al., 2015b), and iv) ultimate analysis (H/C_{org}) (IBI, 2015). ■ Analysis of degree of aromatic condensation by i) instrumental analysis such as ^{13}C NMR (Wiedemeier et al., 2015b), XRD (Lu et al., 2000), NEXAFS (Wiedemeier et al., 2015a) and ii) molecular markers such as BPCA (Wiedemeier et al., 2015a).
O/C _{org} molar ratio	<ul style="list-style-type: none"> ■ Ultimate analysis (EBC, 2012; Spokas, 2010) and XPS analysis (for surface of biochar particles) (Han et al., 2018; Liang et al., 2008).
Thermal/chemical oxidation resistance (labile/stable biochar C determination)	<ul style="list-style-type: none"> ■ Labile/stable biochar C content or (relative) oxidation resistance determined by i) proximate analysis (Crombie et al., 2013; Kusumo et al., 2014), ii) temperature-programmed oxidation (TPO)/thermal oxidation such as thermal degradability (Leifeld, 2007), recalcitrance index R₅₀ (Harvey et al., 2012), and thermal stability indices (TSI) (Suárez-Abelenda et al., 2017), and iii) chemical oxidation such as H₂O₂- and heat-assisted oxidation (Cross and Sohi, 2013) and K₂Cr₂O₇ oxidation (Chen et al., 2016b).
Biotic-abiotic mineralization resistance in soil/incubation and modelling	<ul style="list-style-type: none"> ■ Biochar incubation in soil and mineralization rate modelling to obtain biochar persistence indices such as mean residence time (MRT) (Calvelo Pereira et al., 2014; Singh et al., 2012a), BC₊₁₀₀ (Herath et al., 2015), and half-life time (Bai et al., 2013; Zimmerman, 2010).

the H deficiency ($z = -2c + h$) relative to a saturated species (C_nH_{n+2}). The H deficiency can thus facilitate the calculation of double bond equivalents ($\text{DBE} = -z/2 + n/2 + 1$). DBE is the number of double bonds plus the number of rings. For example, benzene has 4 DBE. The aromatic fraction can be further obtained by normalizing DBE to the molar C and N ($c + n$) contents (Lehmann and Joseph, 2015).

2.3. Chemical compositions

Chemical compositions also play an important role on biochar stability. For instance, the thermally unaltered (feedstock) or partly altered materials, which contain hemicelluloses, cellulose, lipid, protein and lignin, would be labile than the thermally altered chars which comprised mainly of aromatics. Chemical compounds in biochar, such as glycolipids, phospholipids, neutral lipids, and carbohydrates, were found to be the major components which decomposed over the 3.5 years of incubation, while the condensed aromatics remain almost the same during this period (Kuzyakov et al., 2014). That is the reason to convert biochemical compounds in feedstock to stable aromatics in biochar which can be sequestered in soil. The initial biomass is dominated by O- and N-containing functional groups which include carboxylic acids, phenols, alcohols, carbonyls (aldehydes and ketones), amides, amines and heterocycles. These functional groups increase the surface reactivity, and correspondingly decrease the stability of biochar. It is possible that high contents of S and N in biomass and the resultant biochar would have negative effect on biochar stability. These functional groups would react, volatilize, and condense as pyrolysis proceeds, producing liquid bio-oil which is rich in carboxylic acids, phenols, alcohols, amides and amines and solid biochar which is rich in aromatic C structures that are more stable than the starting feedstock (Czernik and Bridgwater, 2004; Mohan et al., 2006).

In addition to the organics, inorganic fractions of biochar such as metal and metal compounds or minerals may also influence the stability of biochar. Carbonates in biochar may be dissolved abiotically under acidic conditions and affect the real carbon sequestration capacity. They can also affect the recalcitrant data (i.e. half-life time) modelled from incubation experiment by CO₂ emissions. Inorganic carbonates contribute significantly to the short-term C mineralization (CO₂ emission) (Fidel et al., 2017). Faster mineralization rates of manure-based biochars than plant-based biochars are believed to be the higher levels of mineral nutrients which can defect the core of biochar C structures of manure-based biochars (Singh et al., 2012a). On the other hand, alkali

and alkaline earth metallic (AAEM) species and other element such as silicon can affect biochar stability. For example, the amorphous silicon within biochar may interact with C to form stable Si-C and enhance the stability of biochar, preventing C from being oxidized (Han et al., 2018).

2.4. Other biochar properties

Other biochar properties such as pore structure and surface area, sorption phenomena, and pH may also be correlated with biochar stability (Lehmann et al., 2011). For example, particle size of biochar can be a significant factor, and therefore, particle size distribution declaration of biochar is required by IBI through dry sieving with 50 mm, 25 mm, 16 mm, 8 mm, 4 mm, 2 mm, 1 mm, and 0.5 mm sieves (IBI, 2015). Fine particle size of biochar may be more susceptible to microbial attack than that of large sized particles (Bruun et al., 2012). The biochar with large particle size may firstly experience reduction on size to enhance its dispersion in the soil by soil fauna (Zimmerman, 2010). The incubation experiments show that the microbial response to biochar is affected by the particle size (Ameloot et al., 2013). The biologic degradation of biochar relies on the activity of extracellular enzymes which have higher activity on smaller particle size (Ameloot et al., 2013). In addition, biochar particle size distribution is related not only to its stability, but also to the transport and interaction of biochar with surroundings during handling, storage, transport, and human exposure (in regard to biochar dust particles) (Aller, 2016).

2.5. Biochar stability assessment

Based on the above-mentioned biochar properties (Table 1) as well as the soil environment that the biochar is applied to, biochar stability can be assessed by several methodologies such as C structures analysis, physicochemical degradation resistance determination, and incubation and modelling (Leng et al., 2019) (Table 2). The C structures such as aromaticity and/or degree of aromatic condensation of biochar may be analyzed by using different techniques (Table 2) such as solid-state ^{13}C NMR (McBeath et al., 2011; Wiedemeier et al., 2015a), XRD (Brown et al., 2006; Keiluweit et al., 2010; Lu et al., 2000), Near-edge X-ray absorption fine structure (NEXAFS) (Wiedemeier et al., 2015a), Mid-infrared spectroscopy (MIR) (Kusumo et al., 2014; Wiedemeier et al., 2015a), X-ray photon spectroscopy (XPS) (Yang et al., 2016), and Fourier transform infrared spectroscopy (FTIR) (Hernandez-Soriano

et al., 2016). Ultimate analysis (e.g., H/C), molecular markers such as benzene polycarboxylic acid (BPCA) (Wiedemeier et al., 2015b) and markers from Pyrolysis-GC-MS (Conti et al., 2016, 2014) and Hydro-Pyrolysis-GC-MS (Rombolà et al., 2016) analysis, and He pycnometry (Wiedemeier et al., 2015b) are also indicators of C structures.

Unlike the C structure and ultimate analyses, which take no account of the effect of other elements on biochar stability, the oxidation resistance stability assessment evaluates the overall oxidation resistance capability of biochar. As shown in Table 1, the oxidation resistance can be quantified by thermal treatment such as proximate analysis (Enders et al., 2012; Klasson, 2017), temperature-programmed oxidation/thermal oxidation (Harvey et al., 2012; Jiang et al., 2016; Zornoza et al., 2016), or by chemical oxidation such as H_2O_2 - and heat-assisted oxidation (Cross and Sohi, 2013), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) oxidation (Chen et al., 2016b) and permanganate oxidation (Calvelo Pereira et al., 2011).

Incubation of biochar in soil with the calculation and modelling of the biochar C mineralization is the most important and fundamental methodology to study the overall biochar stability (Herath et al., 2015; Lehmann and Joseph, 2015; Singh et al., 2012b; Wang et al., 2016; Zimmerman, 2010; Zimmerman et al., 2011). It considers both biotic and abiotic degradation effects on biochar due to the introduction of soil environment. C structure analysis, ultimate analysis, and physico-chemical resistance mentioned above are all based on their correlations with results from biochar incubation and modelling and have been developed as potential biochar stability proxies (Budai et al., 2013; Cross and Sohi, 2013; Harvey et al., 2012; Singh et al., 2012a). These assessment methodologies have been adopted as indicators to study the effect of biochar production variables including biomass feedstock and pyrolysis parameters on biochar stability.

3. Effect of biomass feedstock on biochar stability

3.1. Biochemical compositions

Biomass type or its biochemical compositions may be a decisive factor affecting biochar stability. Due to the crystallinity and polymerization difference, lignin is the most stable component in unaltered biomass, followed by cellulose and hemicelluloses (Li et al., 2017). Higher lignin content in feedstock commonly leads to a higher content of aromatic C in biochar and a slower biochar mineralization rate (Table 3) (Ameloot et al., 2013; Windeatt et al., 2014). Biochar from wood are commonly more stable than those from grasses, sludge and husks (Cely et al., 2014; Hilscher et al., 2009; Zimmerman, 2010). For example, biochar made from palm shell (had the highest typical lignin content) is the most stable among biochars from slow pyrolysis of eight crop residues at 600 °C, while that from wheat straw (had the lowest lignin content) is the least stable (Windeatt et al., 2014). Significantly higher (~10 times) C mineralization rates after 48-day incubation have been reported for rye grass biochars (2.0–3.5%) than those of pine wood biochars (0.2–0.4%) produced under the same pyrolysis conditions (Hilscher et al., 2009). Biochars produced from grasses (10^2 – 10^4 y) have 2–3 orders of magnitude shorter C half-lives than those produced from hard woods (10^5 – 10^7 y) (Zimmerman, 2010). Meta-analysis study (a meta-analysis of 128 observations of biochar-derived CO_2 from 24 studies and biochars derived from more than 20 kinds of feedstocks) also observed similar results as following: the crop-derived biochars decomposes faster (0.025%/day as mean) than grass-derived ones (0.007%/day as mean), while wood-derived biochars has the slowest decomposition rate of 0.004%/day (mean) (Wang et al., 2016).

However, no significant impact on biochar stability was found among different feedstock in several other studies, particularly for biochar produced at high pyrolysis temperature (Conti et al., 2016, 2014; Han et al., 2018; McBeath et al., 2015). The aromaticity/degree of aromatic condensation of biochars from different biomass were

found with no difference at pyrolysis temperature > ~500 °C (Budai et al., 2017; McBeath et al., 2015). The influence of feedstock type on biochar labile C content (H_2O_2 oxidizable fraction) decreased with increasing pyrolysis temperature (from 350 °C to 650 °C), and no significant effect was found on biochar obtained at 650 °C due to the dominant impact of pyrolysis temperature (Crombie and Mašek, 2015). Biochar approaches increasingly similar structures (i.e. mostly poly-aromatic) with increasing temperature. And at higher temperatures, the formation of these structures becomes independent of feedstock type (McBeath et al., 2015). However, the structure changing rate in response to the increasing pyrolysis temperature varied for different biomass (Morales et al., 2015). Therefore, the biochar from low pyrolysis temperature may have diversified stability, while that from high pyrolysis temperature may possibly share a similar stability range for some biomass after most of the labile fractions being removed.

It is worth mentioning that the absolute amount of stable biochar C (overall carbon sequestration potential) will still also depend considerably on the yield of biochar; thus, selection of lignocellulosic biomass of higher lignin content will be preferable as it yields more biochar. Although the stability seems similar for biochar from various feedstocks ($n = 12$) irrespective of their biochemical compositions, carbon sequestration potential which takes into consideration of both stability and yield of biochar correlates closely with the lignin content of feedstocks ($R^2 = 0.78$, $p < 0.004$) (Zhao et al., 2013).

3.2. Inorganic/mineral content

Content of inorganics in biochar can interact with biochar C and may increase or decrease biochar stability depending on mineral species (Table 4) (Xu et al., 2017a). Metals such as K may catalyze the degradation of biochar C during temperature-programmed oxidation (TPO). The reactivity of biochar may be enhanced by AAEM species catalyzed biochar functionalization and therefore decrease of biochar stability (Feng et al., 2018). The pre-washing of biochar to reduce K content from 2173 mg/kg to 171 mg/kg increased significantly biochar stability as indicated by the increase of R_{50} from 0.46 to 0.55 (Windeatt et al., 2014). It is believed that the catalysis effect of water-soluble inorganics on thermal degradation of biochar was removed after water-washing. Gómez et al. (2016) also claimed that water-washing of biochar for reduction of alkali metals effectively avoided the mask of biochar stability as indicated by R_{50} . However, the thermal degradation resistance may not represent oxidative or biotic recalcitrance when studying the effect of minerals on biochar stability. More indices should be used to confirm the effect of AAEM species on biochar stability. Indeed, although the thermal recalcitrance (R_{50}) showed no significant difference between biochar and the corresponding de-ashed biochar, de-ash treatment was found to have positive effect on carbon residence (stable C content) after chemical oxidation by using agents such as $\text{K}_2\text{Cr}_2\text{O}_7$ or H_2O_2 (Yang et al., 2018b).

Additionally, many studies found positive effects of various minerals on biochar stability assessed by chemical oxidation methods (Table 4). The biochar stability is increased with the decrease of H_2O_2 oxidizable fraction in biochar produced from co-pyrolysis of sewage sludge with $\text{Ca}(\text{OH})_2$ (Ren et al., 2017) and also in biochar from co-pyrolysis of rice straw with calcite (CaCO_3) or calcium dihydrogen phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] (Li et al., 2014). The impregnation of biochar with inclusion of Al, Ca, Fe minerals or kaolinite enhanced the H_2O_2 -oxidation resistance of biochar surface because of the formation of organometallic complexes such as $\text{Fe}-\text{O}-\text{C}$, which can prevent biochar $\text{C}-\text{C}/\text{C}=\text{C}/\text{C}-\text{H}$ from being oxidized into $\text{C}-\text{O}$, $\text{C}=\text{O}$, or COOH (Yang et al., 2016). However, the use of chemical oxidation assessment method to study the effect of minerals on biochar stability may also be problematic. Si existence (possibly in the form of Si-C) in biochar resulted in no difference between biochars with high and low/no Si content when H_2O_2 - and heat-assisted oxidation (at high H_2O_2 dose) was used for stability assessment, although higher oxidation

Table 3
Effect of biomass feedstock on biochar stability.

Parameters	Biochar production feedstock, process parameters	Influence (+ / * / -) ^a	Biochar stability assessment methodologies applied to justify the relationship	Refs.
Biomass feedstock (biochemical compositions)	Coconut husk/coconut shell/cotton stalk/olive pomace/palm shell/rice husk/sugarcane bagasse/wheat straw, 600 °C, heating rates, 5 °C/min, retention time, 1 h	+ (lignin content of biomass)	Recalcitrance index R_{50}	Windeatt et al. (2014)
	Pine wood chips/wheat straw/wheat straw pellets, 350/450/550/650 °C, heating rates, 100 °C/min	Indicative	i) H_2O_2 - and heat-assisted oxidation and ii) Mineralized biochar C fraction from incubation	Crombie et al. (2015)
	Pine wood chips/wheat straw/wheat straw pellets, 350/450/550/650 °C, heating rates, 5 °C/min	*	i) H_2O_2 - and heat-assisted oxidation and ii) Mineralized biochar C fraction from incubation	(Crombie and Mašek (2015)
	Wood pellets/straw pellets, 350 °C, residence times, 10/20/40 min, carrier gas flow rates, 0/0.33/0.66 L/min	Indicative	H_2O_2 - and heat-assisted oxidation	
	Wood pellets/straw pellets, 650 °C, residence times, 10/20/40 min, carrier gas flow rates, 0/0.33/0.66 L/min	*	H_2O_2 - and heat-assisted oxidation	
	Corn cobs/Sugar cane bagasse/corn stover/woodchips/corn residues, 500 °C	Indicative	i) H/C and ii) O/C	Carrier et al. (2013)
	Wood/leaf/papermill sludge/poultry litter/cow manure, 400/550 °C	Indicative	Mineralized biochar C fraction and MRT/half-life time assessed by biochar incubation and mineralization rate modelling	Singh et al. (2012a)
	Biochars from 26 studies	+ (lignin content of biomass)	Meta-analysis of biochar mineralization rate from incubation	Wang et al. (2016)
	Vine shoots, 400/500/600 °C, biomass particle size, 0.98/1.97/3.01 cm	+	i) H/C, ii) O/C, and iii) aromaticity analyzed by ^{13}C NMR	Manyà et al. (2014b)
	Switchgrass/pine chips/swine solids/poultry litter, 350 °C, biochar particle size, dust-sized/pelleted-size	+	Mineralized biochar C fraction from incubation	Sigua et al. (2014)
Biomass/biochar particle size	Bamboo sticks, 700 °C, biochar particle size, 0.05/0.05–1.0/1.0–2.0 mm	+	Mineralized biochar C fraction from incubation	Chen et al. (2017)
	Oak/pine/cedar/bubinga/mixed stems and blades of live Eastern gamma grass/sugar cane bagasse, 250/525/650 °C, biochar particle size, < 0.25/0.25–2 mm	+	Mineralized biochar C fraction and half-life time from incubation and mineralization rate modelling	Zimmerman (2010)

^a “+”, “-”, “*” or “*” means positive, negative or limited influence on biochar stability; “indicative” means indicative of influence on biochar stability.

Table 4
Effect of inorganics/minerals on biochar stability.

Inorganics	Source of inorganics	Studied biochar and biochar-inorganic association (for comparison)	Influence (+ / * / -) ^a	Biochar stability assessment methods	Refs.
Water soluble inorganics (mainly K)	Endogenous	Biochar with and without water washing	-	Recalcitrance index R ₅₀	Windeatt et al. (2014)
Water soluble inorganics (mainly K and P)	Endogenous	Biochar with and without water washing	-	Recalcitrance index R ₅₀	Gómez et al. (2016)
Silicon	Endogenous	Biochar has no/low and high content of silicon	+	**H ₂ O ₂ - and heat-assisted oxidation (at low H ₂ O ₂ dose)	Han et al. (2018)
Ash	Endogenous	Biochar with and without de-ash treatment (acid washing)	+	H ₂ O ₂ - and heat-assisted oxidation (at high H ₂ O ₂ dose) i) H ₂ O ₂ - and heat-assisted oxidation and ii) K ₂ Cr ₂ O ₇ oxidation	Yang et al. (2018b)
FeCl ₃ ·6H ₂ O	Exogenous	Biochar and biochar- FeCl ₃ ·6H ₂ O composite	*	Recalcitrance index R ₅₀	Yang et al. (2018b)
Ca(OH) ₂	Exogenous	Biochar from biomass and biochar from co-pyrolysis biomass with Ca(OH) ₂	-	Recalcitrance index R ₅₀	Ren et al. (2017)
CaCO ₃ or Ca(H ₂ PO ₄) ₂ ·H ₂ O	Exogenous	Biochar from biomass and biochar from co-pyrolysis biomass with CaCO ₃ or Ca(H ₂ PO ₄) ₂ ·H ₂ O	+	H ₂ O ₂ - and heat-assisted oxidation	Li et al. (2014)
Kaolinite (Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O)	Exogenous	Biochar from biomass and biochar from co-pyrolysis biomass with Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	+	i) H ₂ O ₂ - and heat-assisted oxidation ii) K ₂ Cr ₂ O ₇ oxidation, iii) aromaticity analyzed by ¹³ C NMR, and iv) biochar C mineralization during incubation i) K ₂ Cr ₂ O ₇ oxidation, ii) aromaticity analyzed by ¹³ C NMR and iii) biochar C mineralization during incubation H ₂ O ₂ - and heat-assisted oxidation	Li et al. (2014)
CaO	Exogenous	Biochar from biomass and biochar from co-pyrolysis biomass with CaO	-	FTIR (reduced oxygenated functional groups)	Wilson et al. (2018)
Attapulgite clay	Exogenous	Biochar from biomass and biochar from co-pyrolysis biomass with attapulgite clay	+	Aromaticity analyzed by ¹³ C NMR	Rafiq et al. (2017)
Silica	Exogenous	Biochar from biomass and biochar from co-pyrolysis biomass with silica	+	i) H/C, ii) O/C molar ratios and ii) thermal degradability	Ahmad et al. (2017)
Kaolinite, AlCl ₃ , FeCl ₃ , or CaCl ₂	Exogenous	Biochar and biochar-kaolinite, AlCl ₃ , FeCl ₃ , or CaCl ₂ composite	+	H ₂ O ₂ - and heat-assisted oxidation	Yang et al. (2016)
Kaolinite	Exogenous	Biochar biochar-kaolinite composite	+	i) K ₂ Cr ₂ O ₇ oxidation and ii) biochar C mineralization during incubation	Yang et al. (2018a)
MgCl ₃ , FeCl ₃ , or CaCl ₂	Exogenous	Biochar and biochar-MgCl ₂ , FeCl ₃ , or CaCl ₂ composite	+	i) H ₂ O ₂ - and heat-assisted oxidation and ii) biochar C mineralization during incubation	Xiao et al. (2018)
Clay minerals such as kaolinite	Exogenous	Biochar incubated in soil of low/no or high content of clay minerals	+	Biochar C mineralization during incubation	Fang et al. (2015)

^a +, *, or “” means positive, negative or limited influence on biochar stability.

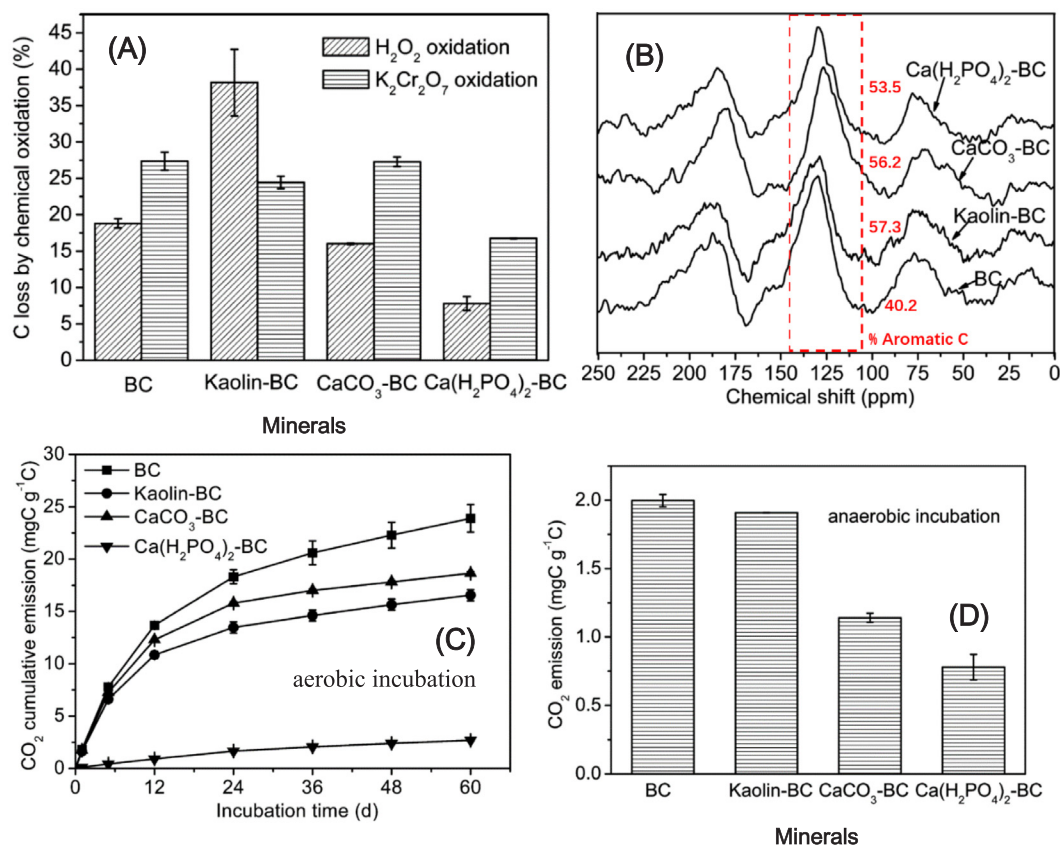


Fig. 3. Effect of minerals on biochar stability assessed by chemical oxidation (A), aromaticity analysis by ¹³C NMR (B), aerobic incubation (C), and anaerobic digestion (D) (Li et al., 2014).

resistance for biochar with high Si was observed at low H₂O₂ dose (Han et al., 2018). In another case, co-pyrolyzing rice straw with kaolin (Al₂O₃·2SiO₂·2H₂O) increased the carbon loss when assessing biochar stability by H₂O₂- and heat-assisted oxidation, although carbon loss from K₂Cr₂O₇ oxidation was reduced (Fig. 4a) (Li et al., 2014). Kaolin-biochar with high surface area allows for the trap of volatiles inside the biochar, which was not readily extracted by deionized water but readily attacked by H₂O₂, resulting in increased C loss (Li et al., 2014). In addition to the methodology difference, these wild results between studies may also be due to the complex mixed effects of these inorganics or the biochar-mineral composites on oxidative properties of biochar.

The effect of the presence of minerals on biochar stability indicated by biochar aromaticity or by results from biochar incubation and modelling can help with the justification of the effect of minerals on biochar stability. Unlike the results from K₂Cr₂O₇ oxidation, both the aromaticity analyzed by ¹³C NMR (Fig. 3b) and biochar C mineralization assessed during aerobic (Fig. 3c) or anaerobic (Fig. 3d) incubation supported the positive effect of minerals on biochar stability (Table 4 and Fig. 3) (Li et al., 2014). Biochar-silica composites have lower H/C and O/C molar ratios and higher thermal stability than the original biochars, suggesting their higher aromaticity and thus higher stability compared to the original ones (Ahmad et al., 2017). Both chemical oxidation (assessed by K₂Cr₂O₇ oxidation) and biological degradation recalcitrance (assessed by incubation) can be enhanced significantly (~50%) by constructing kaolinite-biochar associations (Yang et al., 2018a). Furthermore, mineral salt (MgCl₂, FeCl₃, or CaCl₂) pretreatment of biomass such as manure before pyrolysis was also reported to have increased aromatization and reduced C loss during H₂O₂- and heat-assisted oxidation and CO₂ release during incubation, respectively (Xiao et al., 2018). The increased biochar stability can be explained by enhanced physical protection because of metal-oxygen interaction and

formation of metal mineral phases on biochar surfaces (Xiao et al., 2018).

These findings imply several strategies for enhancing biochar stability (Table 4): i) demetalization of biomass such as the removal of detrimental alkali metals (water-soluble ion) from biomass (Gómez et al., 2016; Windeatt et al., 2014), ii) co-pyrolyzing biomass with such beneficial minerals to produce mineral-rich biochar (Li et al., 2014; Rawal et al., 2016; Ren et al., 2017; Xiao et al., 2018; Xu et al., 2017b), iii) impregnation of biochar with minerals such as kaolinite (Yang et al., 2016; 2018a), and iv) applying biochar in mineral-rich soil (Fang et al., 2014; Purakayastha et al., 2016; Singh et al., 2014) will probably benefit the sequestration of biochar C. However, strategies i) and ii) should be wisely adopted with consideration of the effect of these inorganic minerals on biochar yield. In addition to enhancing biochar stability, some minerals may decrease the biochar yield and the overall carbon sequestration potential (Li et al., 2014) and thus, trade-off between yield and stability should be mediated when choosing these strategies.

Additionally, the observations in these above studies indicate the need of cautiousness when selecting biochar stability assessment methods and the need of assessment method optimization, e.g., the use of thermal/chemical oxidation to assess the stability of biochar with high ash content. Use of biochar incubation experiment, in combination with chemical oxidation or aromaticity analysis, as the stability assessment method is strongly suggested when studying the effect of minerals on biochar stability.

3.3. Particle size

The particle size of biochar is mainly determined by that of feed-stock biomass. Large biomass particle size tends to produce biochar

Table 5
Effect of pyrolysis process parameters on biochar stability.

Parameters	Biochar production feedstock, processing parameters	Influence (+ / * / -) ^a	Biochar stability assessment methodologies applied to justify the relationship	Refs.
Pyrolysis temperature (high temperature treatment, HTT)	Rice straw/pine wood/swine solids/poultry litter, 250/450/600 °C	+	i) H/C, ii) O/C, iii) H ₂ O ₂ - and heat-assisted oxidation (at high H ₂ O ₂ dose), and iv) aromaticity analyzed by ¹³ C NMR	Han et al. (2018)
	Rice straw/swine solids/poultry litter, 250/450/600 °C	*	H ₂ O ₂ - and heat-assisted oxidation (at low H ₂ O ₂ dose)	Harvey et al. (2012)
	12 kinds of biomass feedstock, 200–1050 °C, step size 50/100 °C	+	Recalcitrance index R ₅₀	McBeath et al. (2011)
	Chestnut wood, 200–1000 °C, step size 25/50/100 °C	+	Degree of aromatic condensation (−Δδ) analyzed by ¹³ C NMR	Wiedemeier et al. (2015b)
	Chestnut wood, 500–1000 °C, step size 100 °C	*	Aromaticity analyzed by ¹³ C NMR	
	Chestnut wood/pine wood/fescue grass/rice grass, 100/200–700/1000 °C, step size 100 °C	+	i) H/C, ii) O/C, and iii) degree of aromatic condensation (−Δδ) analyzed by ¹³ C NMR, BPCA markers, and iv) He pycnometry	
	Chestnut wood/pine wood/fescue grass/rice grass, 600–700/1000 °C, step size 100 °C	–	Aromaticity analyzed by BPCA markers and degree of aromatic condensation analyzed by NEXAFS	
	Chestnut wood/pine wood/fescue grass/rice grass, 600–700/1000 °C, step size 100 °C	*	Aromaticity analyzed by ¹³ C NMR	
	Wood chips/rice husk/wheat straw, 350/450/550/650 °C	+	ii) H/C, ii) O/C, iii) proximate analysis, and i) H ₂ O ₂ - and heat-assisted oxidation	Grombie et al. (2013)
	Sugarcane bagasse, 350/450/550 °C	+	H ₂ O ₂ - and heat-assisted oxidation	Gross and Sohi (2013)
	Pine/bark/cornstalk/miscanthus/poplar/switchgrass/Desmodium communis/spirulina/chicken manure/mushroom litter/olive pomace, 400–700 °C, step size 50 °C	+	i) H/C and ii) molecular markers from Pyrolysis-GC-MS	Conti et al. (2016, 2014)
	Corn cob/sawdust/cornstalk, 300/400/500/600 °C	+	ii) H/C and ii) O/C	Liu et al. (2014)
	Oak/pine/cedar/bubinga/Eastern gamma grass/sugar cane bagasse, 250/400/525/650 °C	+	Mineralized biochar C fraction and half-life time from incubation and mineralization rate modelling	Zimmerman (2010)
	Biochars from 35 studies	*	Meta-analysis of biochar mineralization rate obtained from incubation	Wang et al. (2016)
Residence time (heating time at the target pyrolysis temperature)	Pine/bark/cornstalk/miscanthus/poplar/switchgrass/Desmodium communis/spirulina/chicken manure/mushroom litter/olive pomace, 400–700 °C, step size 50 °C	+	i) H/C and ii) molecular markers from Pyrolysis-GC-MS	Conti et al. (2016)
	Switchgrass, 400–700 °C, step size 50 °C, 1/5/10/20 min	+	i) H/C and ii) molecular markers from Pyrolysis-GC-MS	Conti et al. (2014)
	Pig manure/crop residues/municipal solid waste. Biochars were prepared at 300/400/500/700 °C, residence time, 1/2/4/5h	+	Thermal degradability	Zornoza et al. (2016)
	Wheat straw/lignosulfonate, 200/400/600 °C, residence time, 1/2/4h	+	ii) H/C, ii) O/C, and iii) fixed carbon	Zhang et al. (2015)
	Rice straw, 300/400/500/600/700 °C, residence time 1/2/3/5h	*	ii) H/C and O/C, ii) FTIR (functionality), and iii) XRD (atomic structure)	Wu et al. (2012)
	Wood pellets/straw pellets, 350/650 °C, residence times, 10/20/40 min	*	H ₂ O ₂ - and heat-assisted oxidation	Grombie and Mašek (2015)
	Sugarcane bagasse, 350 °C, residence time, 20/40/80 min	+	H ₂ O ₂ - and heat-assisted oxidation	Gross and Sohi (2013)
	Sugarcane bagasse, 550 °C, residence time, 20/40/80 min	*	H ₂ O ₂ - and heat-assisted oxidation	
	Biochar production feedstock, processing parameters	Relationship (+ / * / -) ^a	Biochar stability assessment methodologies applied to justify the relationship	Refs.
	Wheat straw, 525 °C, fast pyrolysis/slow pyrolysis (6 °C/min)	–	Mineralized biochar C fraction from incubation	Brun et al. (2012)
	Poplar wood, 400–600 °C, step size 50 °C, heating rate, 10/20/30 °C/min	*	H/C	Chen et al. (2016a)
	Pine wood chips/wheat straw/wheat straw pellets, 350/450/550/650 °C, heating rates, 5/100 °C/min	*	i) H ₂ O ₂ - and heat-assisted oxidation and ii) Mineralized biochar C fraction from incubation	Grombie et al. (2015)
	Wood chips/rice husk/wheat straw, 350/450/550/650 °C, heating rates, 5/100 °C/min	*	ii) H/C, ii) O/C, iii) proximate analysis, and i) H ₂ O ₂ - and heat-assisted oxidation	Grombie et al. (2013)
	Vine shoots, 400/500/600 °C, pressure, 0.1/0.6/1.1 MPa	+	i) H/C, ii) O/C, and iii) aromaticity analyzed by ¹³ C NMR	Manyà et al. (2014b)
	Miscanthus x giganteus, 550 °C, pressure, 1–26 bar, step size 5 bar	+	i) H/C and ii) aromaticity analyzed by ¹³ C NMR	Melligan et al. (2011)
Reactor type	Olive mill waste, 400/500/600 °C, pressure, 0.1/0.6/1.1 MPa	+	i) H/C, ii) O/C, and iii) aromaticity analyzed by ¹³ C NMR	Manyà et al. (2014a)
	Coconut shells/rice husks/Palmmyra nutshell, 400 °C, reactor type: kiln and drum/cylindrical furnace	Indicative	i) H/C and ii) Mineralized biochar C fraction from incubation	Jegajeevagan et al. (2016)
	willow wood/mixed straw pellets, microwave pyrolysis (170/200 °C)/conventional pyrolysis (200/250/300/350 °C)	Indicative	H ₂ O ₂ - and heat-assisted oxidation	Mašek et al. (2013b)

(continued on next page)

with high yield and large particle size (Table 3). The contact time between the vapor-phase species with the solid would be prolonged in the case of biomass with larger particles, and thus enhance the secondary reactions and result in additional formation of carbon through re-polymerization, leading to higher fixed-carbon yield (Manyà et al., 2014b). Therefore, pyrolysis of biomass with larger particles at higher peak temperatures leads to the production of more stable materials. The stability of the vine shoots-derived biochar analyzed by either aromaticity (NMR) or molar ratios of O/C and H/C depends mainly on biomass particle size, and larger size means more stable (Manyà et al., 2014b). The mineralization rate of larger-size biochar was also observed to be lower than that of smaller-size biochar (Chen et al., 2017; Sigua et al., 2014; Zimmerman, 2010). Zimmerman (2010) reported that the mineralization rates of biochar C of fine biochar (particle size < 0.25 mm) during incubation (1 year) are about 1.5 times greater than that of the coarse fraction (> 0.25 mm). The amount of CO₂ evolved from biochar during incubation (50 days) in two different soils varies significantly between biochars with different particle sizes (dust with size < 0.42 mm and pellet with size > 2 mm) ($p \leq 0.0001$), with considerably higher CO₂ evolution found for pellet (Sigua et al., 2014).

However, biomass with too large particle size would result in incomplete carbonization and thus low biochar stability, and the preferable size of biomass for pyrolysis is mainly depend on the types of pyrolysis reactor (Kan et al., 2016; Tripathi et al., 2016). The size of feedstock required for pyrolysis ranges from < 0.2 to 6 mm for rotating cone and < 2 mm for bubbling fluidized bed (< 6 mm for circulating fluidized bed) to 5–50 mm for heated kiln, auger/screw feed, and vacuum, and to < 20 mm for ablative reactor (Kan et al., 2016). Other process parameters may also affect the biochar particle size. For example, fast pyrolysis produces fine dust or powder biochars, whereas continuous slow pyrolysis technologies generate biochar with larger particles up to several centimeters in dimension (Aller, 2016).

4. Effect of pyrolysis parameters on biochar stability

4.1. Pyrolysis temperature

Pyrolysis temperature during biochar production is the most significant factor that affects the aromaticity and aromatic condensation and determines the stability of biochar. Many studies found that as the pyrolysis temperature increasing, the content of stable fused aromatic ring structures increases, while that of the labile non-aromatic structures decreases in dimension and quantity (Table 5). With increasing pyrolysis temperature, contents of macromolecules such as hemicellulose, cellulose, lignin, protein and polysaccharides in solid residue decrease, whereas isolated aromatic rings begin to form (Keiluweit et al., 2010; Suárez-Abelenda et al., 2017). Further increasing pyrolysis temperature results in small and 'defective' sheets of condensed aromatic rings which can stack up to form so-called turbostratic crystallites (Fig. 4) (Keiluweit et al., 2010). Fig. 4 shows the biochar structure progressed from microcrystalline cellulose (plant material, at pyrolysis temperature < 200 °C) to turbostratic crystallites through four distinct categories of char: (1) transition chars (from 200 °C to 300 °C with dehydration continues together with the loss of volatile matter caused by depolymerization of plant biopolymers), (2) amorphous chars (from > 300 °C to 600 °C with a predominance of small aromatic units arranged in random order and the original biomass structure is almost totally depolymerized), (3) composite char (from 600 °C to 700 °C with biomass carbonization being the dominant process), and (4) turbostratic char (pyrolysis temperature > 700 °C carbonization with more ordered carbonaceous structures with a larger more ordered graphene-like sheets) (Aller, 2016; Keiluweit et al., 2010). The transformation of feedstock materials to form increasingly carbonized/aromatized structures contributes greatly to the environmental recalcitrance of biochar (Harvey et al., 2012; Keiluweit et al., 2010).

Significantly positive influence of pyrolysis temperature on biochar

Table 5 (continued)

Parameters	Biochar production feedstock, processing parameters	Influence (+ / - / *) ^a	Biochar stability assessment methodologies applied to justify the relationship	Refs.
Carrier gas	Wood pellets/straw pellets, 350/650 °C, residence times, 10/20/40 min, carrier gas flow rates, 0/0.33/0.66 L/min corn stover/vine shoots/two-phase olive mill waste, carrier gas, N ₂ /CO ₂	* *	H ₂ O ₂ - and heat-assisted oxidation i) H/C, ii) O/C, iii) Recalcitrance index R ₉₀ , and iv) H ₂ O ₂ - and heat-assisted oxidation	Crombie and Mašek (2015) Manyà et al. (2018)

^a “+”, “-”, or “*” means positive, negative or limited influence on biochar stability; “indicative” means indicative of influence on biochar stability.

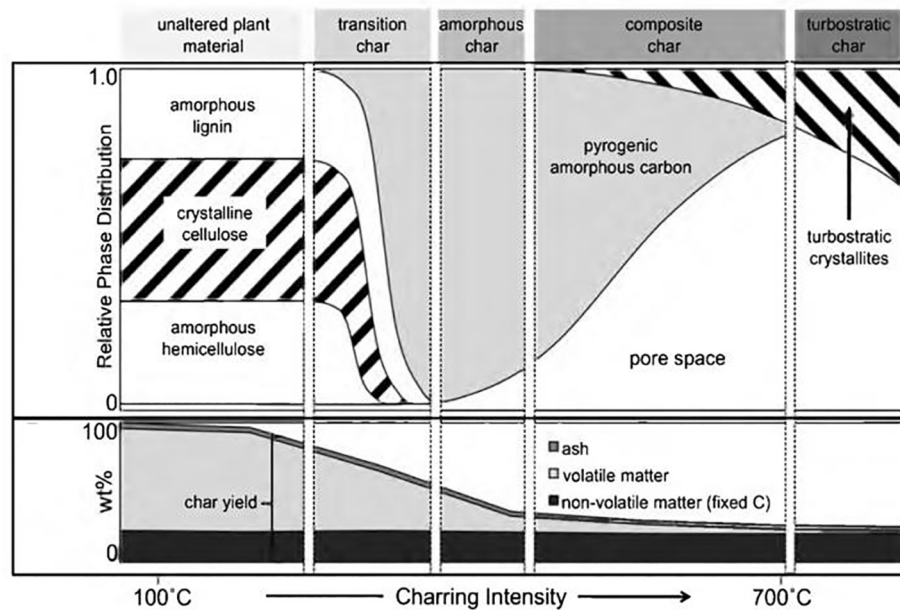


Fig. 4. Progressive biochar structure transformation as the increasing heat treatment temperature (HTT). Reprinted from (Keiluweit et al., 2010).

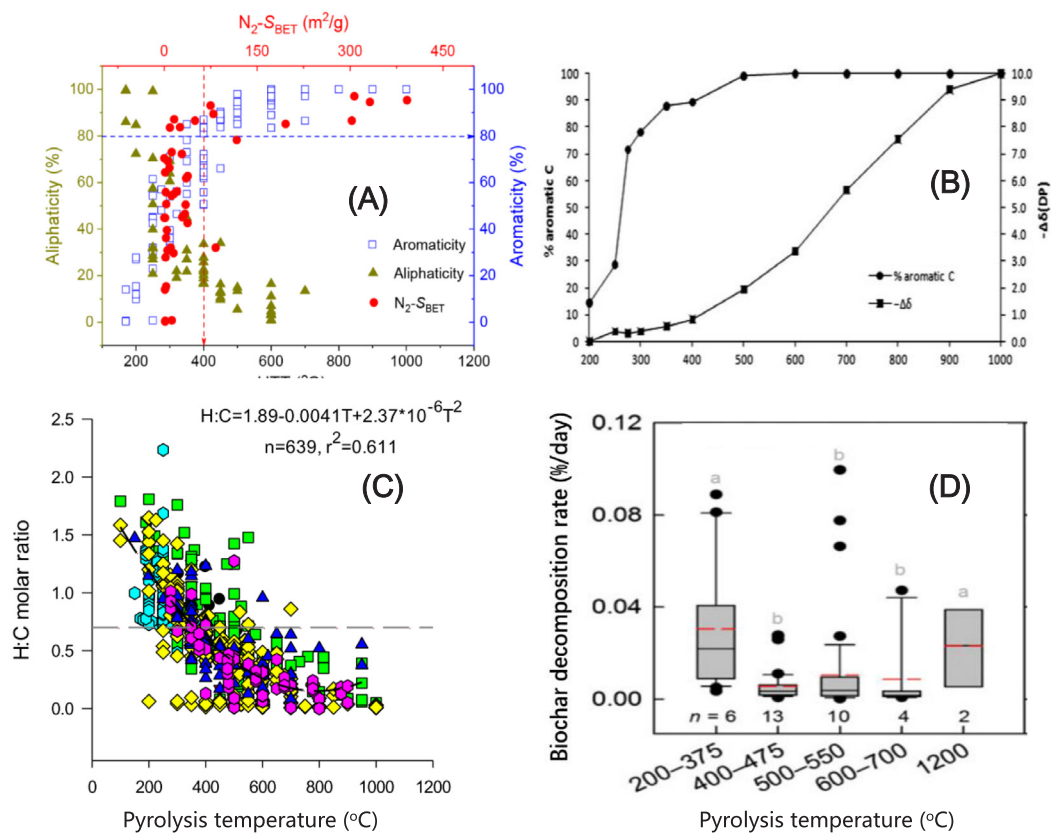


Fig. 5. Correlations between high temperature treatment (HTT)/pyrolysis temperature and aromaticity analyzed by ^{13}C Nuclear magnetic resonance spectroscopy (NMR) (A) (Lian and Xing, 2017), HTT and aromaticity (% aromatic C)/degree of aromatic condensation ($-\Delta\delta$) analyzed by ^{13}C NMR (B) (McBeath et al., 2011), HTT and H/C mole ratio (C) (Aller, 2016), and between HTT and decomposition rate (D) (Wang et al., 2016).

stability is found in almost all studies irrespective of the experimental conditions and stability assessment method (Table 5 and Fig. 5). The correlations between pyrolysis temperature and H/C ($R^2 = 0.611$, $n = 639$) (Aller, 2016), aromaticity (Lian and Xing, 2017), and mineralization rate during incubation (Wang et al., 2016) are quite indicative of the strong positive influence of pyrolysis temperature on

biochar stability. The modelled carbon half-life of the oak biochar produced at 250°C (840 years) was found much lower than that of the oak biochar produced at 650°C (4.0×10^7 years) (Zimmerman, 2010). It is worth mentioning that although Mašek et al. (2013) also obtained higher oxidative stability for biochar produced at higher pyrolysis temperature, the yield of stable biochar fraction (the total mass of the

stable biochar) that can possibly be sequestered in long-term is, nevertheless, nearly independent of the temperature as the biochar yield decreased as the incremental temperature. A trade-off between reduced biochar yield and increased stable C content with increasing temperature is generally optimized between pyrolysis temperature 500 and 700 °C for most feedstock (observed from the results of 17 kinds of biomass type in pyrolysis temperature range of 300–900 °C) (McBeath et al., 2015). Therefore, the optimization of pyrolysis temperature should aim at biochar production of both high yield and stability without sacrificing the C sequestration potential (Crombie et al., 2013; Mašek et al., 2013a). Zhao et al. (2013) found that biochar stability is mainly determined by pyrolysis temperature (200–650 °C), while the potential total C sequestration capacity (product stability combined with stable C yield) depends more on feedstock ($n = 12$).

Pyrolysis temperature is not the only determining factor affecting biochar stability. Biochar produced at higher pyrolysis temperature may not necessarily have higher stability in comparison to that produced at lower pyrolysis temperature. Other influencing factors such as biomass feedstock compositions and properties may overpass pyrolysis temperature and result in different biochar stability sequence (Han et al., 2018). The results from meta-analysis study from ref. (Wang et al., 2016) show the combined effects of all influencing factors, including biomass feedstock and process parameter difference (reviewed in this study), soil and environment difference, and incubation experiment design and modelling difference, on biochar stability. Therefore, dramatic biochar C mineralization rate differences were observed for biochar obtained at the same temperature ranges (Wang et al., 2016). However, the less indicative of the positive effect of pyrolysis temperature on biochar stability reported in refs. (Wiedemeier et al., 2015b) and (McBeath et al., 2011) (Table 5) is because of the incapability of the biochar stability assessment methodologies applied. Aromaticity analysis is less capable to discriminate from each other of biochars produced at high pyrolysis temperature (e.g., > 600 °C) (Lian and Xing, 2017; McBeath et al., 2011; Wiedemeier et al., 2015b). The results of the degree of aromatic condensation should be more convincing (Table 5 and Fig. 5B) (McBeath et al., 2011).

4.2. Reaction residence time

Reaction residence time may affect the carbonization degree and yield of biochar especially at low temperature. The holding time at the target pyrolysis temperature can play a critical role in the carbonization efficiency, particularly in the cases where the heat transfer limitations are not negligible. Increasing kiln residence time from 20 to 80 min significantly increased stability for the biochar produced at 350 °C (Cross and Sohi, 2013). Longer residence time during pyrolysis resulted in more carbonized biochars, which have less labile organic matter and are less vulnerable to microbial attack (Zornoza et al., 2016). Higher thermal oxidative stability was found for biochar produced from manure, crop residues, and municipal solid waste at temperature 300–700 °C with longer reaction residence time (residence time range 1–5 h) (Zornoza et al., 2016). Shorter residence time is believed to contribute to the higher rates of biochar C mineralization in soil (Nguyen et al., 2009; Singh et al., 2012a). However, no significant effect of residence time was found at pyrolysis temperature 550 °C, suggesting a trade-off between pyrolysis temperature and kiln residence time for the completion of carbonization to produce biochar with high stability (Cross and Sohi, 2013). The effect of residence time is often dominated by the pyrolysis temperature and it is sometimes hard to give a straight forward idea about the role of residence time on biochar stability (Tripathi et al., 2016).

4.3. Heating rate

Both of slow pyrolysis and fast pyrolysis can be used for production of biochar, although slow pyrolysis is more commonly used. Slow

pyrolysis is carried out in the absence of oxygen at temperatures 350–600 °C using slow heating rates and long residence times (several hours or even days); fast pyrolysis is performed at high temperature process in which small biomass particles are rapidly heated (in seconds or minutes) in the absence of oxygen. Biochar yield is significantly affected by heating rate; lower heating rates lead to higher yields (Windeatt et al., 2014).

Heating rate may have effect on biochar stability, and low heating rate may be favorable. Lower heating rate may result in longer time for the dominating effect of pyrolysis temperature on biochar stability particularly at high temperature (e.g., 650 °C) (Crombie et al., 2015). The lower heating rate (24 °C/min) can facilitate aromatic structures formation in biochar than the higher heating rate (62 °C/min) (Calvelo Pereira et al., 2011). Low heating rate favors the retention of structural complexity, while loss of structural complexity would happen at high heating rate because of the local melting of cell structures, phase transformations and swelling (Cetin et al., 2004; Lehmann and Joseph, 2015). Smaller ring clusters were found in biochars produced at higher heating rates with some feedstocks remaining unaltered (Sun et al., 2012).

However, low heating rate does not necessarily mean higher biochar stability. Heating rate range of 5–20 °C/min during pyrolysis was found with no statistical effect ($P > 0.5$) on fixed C, volatile matter, stable C and O/C ratio (Cross and Sohi, 2013). Crombie et al. (2013) also found that the heating rate (across the wide range of 1–100 °C/min) shows no notable impact on the concentration of stable C in biochar, although a slight decline of stable C yields in biochar from high heating rate could be discerned. At high pyrolysis temperature, the low heating rate (e.g., 5 °C/min) leads to long duration of chemical reactions occurring during pyrolysis which results in long time for the dominating effect of pyrolysis temperature on biochar stability causing similar stable biochar C contents to be obtained (Crombie et al., 2015). Considering both of biochar yield and stability, low heating rate is always favorable although it is more time-consuming.

4.4. Pyrolysis pressure

Pyrolysis is commonly carried out under non- or low-pressurized conditions. The effect of pyrolysis pressure on biochar stability was studied by only several researchers. Higher pressures and the absence of ventilation prolong intraparticle residence time of pyrolyzing vapors and increase the rate of decomposition reactions, and thus promote the formation of char and gas at the expense of condensable organic vapors (Lehmann and Joseph, 2015).

Increasing the pyrolysis pressure from atmospheric to 5, 10 and 20 bars leads to the formation of biochar with larger particles and the decrease of char activity (Cetin et al., 2004), which may indirectly influence the stability of biochar. Biochar with larger particle size and modified surface shape is obtained at higher pressures, and the particle size difference can also contribute to biochar stability (Cetin et al., 2004). Melligan et al. (2011) observed an increase of aromatic carbon content with pressure increasing from atmospheric to 26 bar. Similar increase trend of aromatic carbon was also observed when the pressure was increased from 0.1 to 1.1 MPa in the pyrolysis of vine shoots or olive mill waste (Manyà et al., 2014a,b). Therefore, pressurized pyrolysis favors the production of biochar with high stability, and most probably also with high biochar yield.

4.5. Pyrolysis reactor type

Few studies investigated the effect of reactor configurations on biochar stability, although the available results indicate dramatic difference between biochar produced from kiln & drum and lab cylindrical furnace. Jegajeevagan et al. (2016) prepared biochar from three feedstocks with kiln & drum and lab furnace as the pyrolyzer, respectively. As evidenced by the lower H/C ratio (0.17–0.44 vs. 0.63–0.73) and

mineralization rate (15.5–34.7 mg mineralized C/kg soil vs. 12.2–91.6 mg mineralized C/kg soil), the kiln & drum-based biochar has noticeably higher stability than that from lab furnace (Jegajeevagan et al., 2016). Therefore, the authors claimed that the biodegradability results (stability) of biochar produced from controlled pyrolysis (lab-produced using modern pyrolyzers) is probably not applicable to artisanally charred one, although the artisanal method (such as kiln & drum) is most likely to be the biochar production method that will be used in developing countries (Jegajeevagan et al., 2016). More studies should be carried out to investigate the performance of traditional kiln on the properties of biochar. Considering that traditional kiln is generally inefficient and polluting with CH₄, CO, and particulates emissions (Sparrevik et al., 2015), modification of pyrolyzer would be preferable. A recent study shows that a pilot-scale retort kiln which recirculates the syngas produced from pyrolysis is very robust to produce biochar of high stability; biochar with H/C_{org} ratio of 0.12–0.13 of was obtained using corncob and eucalyptus tree bark as the feedstock (Djousse Kanouo et al., 2018). Unsatisfactorily, no comparison with biochar produced by modern pyrolyzers was made in this study.

On the other hand, there are many types of modern reactor available in addition to cylindrical furnace, e.g., fluidized bed reactors, circulating bed reactors, ablative reactors, entrained flow reactors, and microwave pyrolyzer, they may produce biochar with different stability and it is worthy to make further effort. For example, microwave pyrolysis which heat biomass with microwave, rather than heat with hot gases or solid heat carrier like the other pyrolysis reactors do, can produce biochar with higher stability (Mašek et al., 2013b). This may be due to the better aromatization performance of microwave pyrolysis; lower cellulose content was observed for biochar produced from microwave pyrolysis than that derived from conventional pyrolysis at similar pyrolysis temperature (Mašek et al., 2013b).

5. Perspectives

5.1. Major influencing process parameters

Biochar stability is influenced by biomass feedstock (e.g., biochemical compositions, content of inorganics, and particle size) and production conditions (e.g., pyrolysis temperature, reaction residence time, heating rate, pressure, and reactor). Pyrolysis temperature is the dominant parameter for biochar stability and then follows the biochemical compositions and inorganic mineral contents of biomass. Generally, high pyrolysis temperature and the use of high-lignin biomass with high mineral content are preferable for production of biochar with high stability. Pyrolysis of biomass with high content of minerals and co-pyrolysis of biochar with mineral also probably lead to high-stability biochar. Alternatively, biochar produced after pyrolysis can be impregnated with minerals to enhance the stability. Multiple biochar stability assessment methods should be used in combination to justify the influence of process parameters on biochar stability. The assessment methods include ultimate analysis (H/C_{org} and O/C_{org}), proximate analysis, aromaticity and degree of aromatic condensation, oxidation resistance, and incubation & modelling.

5.2. Trade-off between biochar yield and stability

High pyrolysis temperature will most likely to reduce biochar yield. Some minerals can also affect biochar yield. Considering that both the yield and stability of biochar contribute greatly to carbon sequestration capacity (the total carbon that can be stored) of biochar, the production of biochar with high stability by optimizing processing parameters is suggested not to sacrifice heavily the biochar yield (particularly when optimizing pyrolysis temperature). It should be bear in mind that the decrease of biochar yield would most probably result in the increased release of biomass C to atmosphere in the form of CO₂ during processing. The concentration of stable C in biochar will stay stable beyond a

certain temperature threshold while biochar yield continues to decrease. Pyrolysis temperature 400–700 °C is recommended for biochar production depending on feedstock. Satisfactorily, long reaction residence time, slow heating rate, high pressure, and biomass feedstock of high-lignin content with large particle size will be preferable for both yield and stability of biochar and contribute to high carbon sequestration capacity. Nevertheless, these factors will lose their contribution when pyrolysis temperature increases to values high enough (i.e. > ~500 °C, vary depending on biomass feedstock) to dominate the effect of pyrolysis on biochar stability.

5.3. Other process parameters may have effect on biochar stability

There are many other pyrolysis parameters that may have effects on stability of biochar, which include the presence of active reagents (steam, CO₂, O₂, etc.), the flow rate of inert carrier gas, reactor configurations, and mode of operation [intermittent operation (batch), nearly continuous, continuous], etc. Future researches need also to focus on the influence of these factors on the stability of biochar.

5.4. Trade-offs between biochar yield & stability and other biochar properties to achieve climate change mitigation

Practically, other biochar properties such as C/N ratio, liming effect, and N-containing compounds sorption capability, in addition properties related to biochar yield and stability, can also contribute significantly to climate change mitigation by altering the emissions of soil-derived GHGs such as N₂O, which is the dominant ozone-depleting substance emitted in the 21st century (Ravishankara et al., 2009). The reported diversified effect of biochar on soil GHGs emissions because of biochar property difference warrant further effort. For example, in a meta-analysis study, both of biomass type and pyrolysis temperature were identified to have significant influence on soil N₂O emissions (Cayuela et al., 2014).

5.5. Trade-offs between climate change mitigation and the improvement on soil and crops

Biochar as a climate change mitigation tool will less likely to act alone. Most probably, the simultaneous climate change mitigation and soil remediation/amendment with or without crop production enhancement would be implemented. For example, the mission of the IBI is to test and use biochar for simultaneous soil fertility enhancement and climate change mitigation. On the other hand, without considering biochar C mineralization and the effect biochar on soil GHGs emissions, the use of biochar as soil enhancer may induce intense short-term GHGs emissions particularly when biochar produced at low pyrolysis temperature is applied. During the studies on the use of biochar either for climate change mitigation or for soil enhancement or for both, more properties, e.g., content of nutrients such as K, P, and micro-nutrient elements, content of toxic/inhibitory compounds such as heavy metals, cation exchange capacity, water-holding capacity, density, pH, and liming effect, should be considered and are suggested to be reported as many as possible in future investigations to facilitate the comprehensive assessment of biochar.

In addition to synergies between soil fertility enhancement and climate change mitigation, there are other potential wins which also worth considering including biofuel/bioenergy production, pollutant immobilization, and waste disposal.

6. Conclusions

Biochar production parameters including biomass compositions and properties and pyrolysis conditions affect biochar stability differently. Pyrolysis temperature is the dominant parameter determines biochar stability. At high temperature (e.g., > 500 °C), biochar of similar

structures (high aromaticity) can be produced and biochar stability is independent of biomass type and other pyrolysis conditions. At relative low temperature, the influence of other process parameters may become prominent; long reaction residence time, slow heating rate, high pressure, co-pyrolysis with beneficial minerals, biomass feedstock of high-lignin content and large particle size are preferable to enhance biochar stability.

Acknowledgements

The study was supported by the National Natural Science Foundation of China (Nos. 51808278 and 21707056).

References

- Ahmad, M., Ahmad, M., Usman, A.R.A., Al-Faraj, A.S., Abduljabbar, A., Ok, Y.S., Al-Wabel, M.I., 2017. Date palm waste-derived biochar composites with silica and zeolite: synthesis, characterization and implication for carbon stability and recalcitrant potential. *Environ. Geochem. Health* 1–18.
- Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere* 99, 19–33.
- Aller, M.F., 2016. Biochar properties: transport, fate, and impact. *Crit. Rev. Environ. Sci. Technol.* 46, 1183–1296.
- Ameloot, N., Graber, E.R., Verheijen, F.G.A., De Neve, S., 2013. Interactions between biochar stability and soil organisms: review and research needs. *Eur. J. Soil Sci.* 64, 379–390.
- Bai, M., Wilske, B., Buegger, F., Esperschütz, J., Kammann, C.I., Eckhardt, C., Koestler, M., Kraft, P., Bach, M., Frede, H.G., Breuer, L., 2013. Degradation kinetics of biochar from pyrolysis and hydrothermal carbonization in temperate soils. *Plant Soil* 372, 375–387.
- Brown, R.A., Kercher, A.K., Nguyen, T.H., Nagle, D.C., Ball, W.P., 2006. Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. *Org. Geochem.* 37, 321–333.
- Bruun, E.W., Ambus, P., Eggsgaard, H., Haugaard-Nielsen, H., 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. *Soil Biol. Biochem.* 46, 73–79.
- Budai, A., Calucci, L., Rasse, D.P., Strand, L.T., Pengerud, A., Wiedemeier, D., Abiven, S., Forte, C., 2017. Effects of pyrolysis conditions on *Miscanthus* and corn cob chars: characterization by IR, solid state NMR and BPCA analysis. *J. Anal. Appl. Pyrol.* 128, 335–345.
- Budai, A., Zimmerman, A.R., Cowie, A.L., Webber, J.B.W., Singh, B.P., Glaser, B., Masiello, C.A., Andersson, D., Shields, F., Lehmann, J., Camps Arbestain, M., Williams, M., Sohi, S., Joseph, S., 2013. Biochar carbon stability test method: an assessment of methods to determine biochar carbon stability [WWW Document]. IBI Doc. Carbon Methodol. Int. Biochar. Initiat.
- Calvelo Pereira, R., Camps Arbestain, M., Kaal, J., Vazquez Sueiro, M., Sevilla, M., Hindmarsh, J., 2014. Detailed carbon chemistry in charcoals from pre-European Māori gardens of New Zealand as a tool for understanding biochar stability in soils. *Eur. J. Soil Sci.* 65, 83–95.
- Calvelo Pereira, R., Kaal, J., Camps Arbestain, M., Pardo Lorenzo, R., Aitkenhead, W., Hedley, M., Macias, F., Hindmarsh, J., Maciá-Agulló, J.A., 2011. Contribution to characterisation of biochar to estimate the labile fraction of carbon. *Org. Geochem.* 42, 1331–1342.
- Carrier, M., Joubert, J.E., Danje, S., Hugo, T., Görgens, J., Knoetze, J.H., 2013. Impact of the lignocellulosic material on fast pyrolysis yields and product quality. *Bioresour. Technol.* 150, 129–138.
- Cayuela, M.L., van Zwieten, L., Singh, B.P., Jeffery, S., Roig, A., Sánchez-Monedero, M.A., 2014. Biochar's role in mitigating soil nitrous oxide emissions: a review and meta-analysis. *Agric. Ecosyst. Environ.* 191, 5–16.
- Cely, P., Tarquis, A.M., Paz-Ferreiro, J., Méndez, A., Gascó, G., 2014. Factors driving the carbon mineralization priming effect in a sandy loam soil amended with different types of biochar. *Solid Earth* 5, 585–594.
- Cetin, E., Moghtaderi, B., Gupta, R., Wall, T.F., 2004. Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars. *Fuel* 83, 2139–2150.
- Chen, D., Li, Y., Cen, K., Luo, M., Li, H., Lu, B., 2016a. Pyrolysis polygeneration of poplar wood: effect of heating rate and pyrolysis temperature. *Bioresour. Technol.* 218, 780–788.
- Chen, D., Yu, X., Song, C., Pang, X., Huang, J., Li, Y., 2016b. Effect of pyrolysis temperature on the chemical oxidation stability of bamboo biochar. *Bioresour. Technol.* 218, 1303–1306.
- Chen, J., Li, S., Liang, C., Xu, Q., Li, Y., Qin, H., Fuhrmann, J.J., 2017. Response of microbial community structure and function to short-term biochar amendment in an intensively managed bamboo (*Phyllostachys praecox*) plantation soil: effect of particle size and addition rate. *Sci. Total Environ.* 574, 24–33.
- Chen, M., Zeng, G., Zhang, J., Xu, P., Chen, A., Lu, L., 2015. Global landscape of total organic carbon, nitrogen and phosphorus in lake water. *Sci. Rep.* 5, 15043.
- Conti, R., Fabbri, D., Vassura, I., Ferroni, L., 2016. Comparison of chemical and physical indices of thermal stability of biochars from different biomass by analytical pyrolysis and thermogravimetry. *J. Anal. Appl. Pyrol.* 122, 160–168.
- Conti, R., Rombolà, A.G., Modelli, A., Torri, C., Fabbri, D., 2014. Evaluation of the thermal and environmental stability of switchgrass biochars by Py-GC-MS. *J. Anal. Appl. Pyrol.* 110, 239–247.
- Crombie, K., Mašek, O., 2015. Pyrolysis biochar systems, balance between bioenergy and carbon sequestration. *GCB Bioenergy* 7, 349–361.
- Crombie, K., Mašek, O., Cross, A., Sohi, S., 2015. Biochar - synergies and trade-offs between soil enhancing properties and C sequestration potential. *GCB Bioenergy* 7, 1161–1175.
- Crombie, K., Mašek, O., Sohi, S.P., Brownsort, P., Cross, A., 2013. The effect of pyrolysis conditions on biochar stability as determined by three methods. *GCB Bioenergy* 5, 122–131.
- Cross, A., Sohi, S.P., 2013. A method for screening the relative long-term stability of biochar. *GCB Bioenergy* 5, 215–220.
- Czernik, S., Bridgwater, A.V., 2004. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* 18, 590–598.
- Djousse Kanouo, B.M., Allaire, S.E., Munson, A.D., 2018. Quality of biochars made from eucalyptus tree bark and corn cob using a pilot-scale retort kiln. *Waste Biomass Valorization* 9, 899–909.
- EBC, 2012. European Biochar Certificate - Guidelines for a Sustainable Production of Biochar. European Biochar Foundation (EBC), Arbaz, Switzerland Version 6.3E of 14th August 2017.
- Enders, A., Hanley, K., Whitman, T., Joseph, S., Lehmann, J., 2012. Characterization of biochars to evaluate recalcitrance and agronomic performance. *Bioresour. Technol.* 114, 644–653.
- Fang, Y., Singh, B., Singh, B.P., 2015. Effect of temperature on biochar priming effects and its stability in soils. *Soil Biol. Biochem.* 80, 136–145.
- Fang, Y., Singh, B., Singh, B.P., Krull, E., 2014. Biochar carbon stability in four contrasting soils. *Eur. J. Soil Sci.* 65, 60–71.
- Feng, D., Zhao, Y., Zhang, Y., Xu, H., Zhang, L., Sun, S., 2018. Catalytic mechanism of ion-exchanging alkali and alkaline earth metallic species on biochar reactivity during CO₂/H₂O gasification. *Fuel* 212, 523–532.
- Fidel, R.B., Laird, D.A., Parkin, T.B., 2017. Impact of biochar organic and inorganic carbon on soil CO and NO emissions. *J. Environ. Qual.* 46, 505.
- Gómez, N., Rosas, J.G., Singh, S., Ross, A.B., Sánchez, M.E., Cara, J., 2016. Development of a gained stability index for describing biochar stability: relation of high recalcitrance index (R50) with accelerated ageing tests. *J. Anal. Appl. Pyrol.* 120, 37–44.
- Han, L., Ro, K.S., Wang, Y., Sun, K., Sun, H., Libra, J.A., Xing, B., 2018. Oxidation resistance of biochars as a function of feedstock and pyrolysis condition. *Sci. Total Environ.* 616–617, 335–344.
- Harvey, O.R., Kuo, L., Zimmerman, A.R., Louchouart, P., Amonette, J.E., Herbert, B.E., 2012. An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars). *Environ. Sci. Technol.* 46, 1415–1421.
- Herath, H.M.S.K., Camps-Arbestain, M., Hedley, M.J., Kirschbaum, M.U.F., Wang, T., van Hale, R., 2015. Experimental evidence for sequestering C with biochar by avoidance of CO₂ emissions from original feedstock and protection of native soil organic matter. *GCB Bioenergy* 7, 512–526.
- Hernandez-Soriano, M.C., Kerré, B., Kopittke, P.M., Horemans, B., Smolders, E., 2016. Biochar affects carbon composition and stability in soil: a combined spectroscopy-microscopy study. *Sci. Rep.* 6, 25127.
- Hilscher, A., Heister, K., Siewert, C., Knicker, H., 2009. Mineralisation and structural changes during the initial phase of microbial degradation of pyrogenic plant residues in soil. *Org. Geochem.* 40, 332–342.
- Huang, H., Yuan, X., 2015. Recent progress in the direct liquefaction of typical biomass. *Prog. Energy Combust. Sci.* 49, 59–80.
- IBI, 2015. Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil. Int. Biochar Initiat.
- Jegajevagan, K., Mabilde, L., Gebremikael, M.T., Ameloot, N., De Neve, S., Leinweber, P., Sleutel, S., 2016. Artisanal and controlled pyrolysis-based biochars differ in biochemical composition, thermal recalcitrance, and biodegradability in soil. *Biomass Bioenergy* 84, 1–11.
- Jiang, L., Yuan, X., Li, H., Chen, X., Xiao, Z., Liang, J., Leng, L., Guo, Z., Zeng, G., 2016. Co-pelletization of sewage sludge and biomass: thermogravimetric analysis and ash deposits. *Fuel Process. Technol.* 145, 109–115.
- Kan, T., Strezov, V., Evans, T.J., 2016. Lignocellulosic biomass pyrolysis: a review of product properties and effects of pyrolysis parameters. *Renew. Sustain. Energy Rev.* 57, 126–1140.
- Keiluweit, M., Nico, P.S., Johnson, M.G., Kleber, M., 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ. Sci. Technol.* 44, 1247–1253.
- Klasson, K.T., 2017. Biochar characterization and a method for estimating biochar quality from proximate analysis results. *Biomass Bioenergy* 96, 50–58.
- Kuhlbusch, T.A.J., 1995. Method for determining black carbon in vegetation fire residues. *Environ. Sci. Technol.* 29, 2695–2702.
- Kusumo, B., Arbestain, M., Mahmud, A., Hedley, M., Hedley, C., Pereira, R., Wang, T., Singh, B., 2014. Assessing biochar stability indices using near infrared spectroscopy. *J. Near Infrared Spectrosc.* 22, 313–328.
- Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific ¹⁴C analysis. *Soil Biol. Biochem.* 70, 229–236.
- Lai, F., Chang, Y., Huang, H., Wu, G., Xiong, J., Pan, Z., Zhou, C., 2018. Liquefaction of sewage sludge in ethanol-water mixed solvents for bio-oil and biochar products. *Energy* 148, 629–641.
- Lehmann, J., 2007a. Bio-energy in the black. *Front. Ecol. Environ.* 5, 381–387.
- Lehmann, J., 2007b. A handful of carbon. *Nature* 447, 143–144.
- Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems - A review. *Mitig. Adapt. Strateg. Glob. Chang.* 11, 403–427.

- Lehmann, J., Joseph, S. (Eds.), 2015. *Biochar for Environmental Management: Science, Technology and Implementation*, second ed. Routledge, London and New York.
- Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011. Biochar effects on soil biota – A review. *Soil Biol. Biochem.* 43, 1812–1836.
- Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P., Krull, E., 2008. Australian climate-carbon cycle feedback reduced by soil black carbon. *Nat. Geosci.* 1, 832–835.
- Leifeld, J., 2007. Thermal stability of black carbon characterised by oxidative differential scanning calorimetry. *Org. Geochem.* 38, 112–127.
- Leng, L., Huang, H., Li, H., Li, J., Zhou, W., 2019. Biochar stability assessment methods: a review. *Sci. Total Environ.* 647, 210–222.
- Leng, L., Li, H., Yuan, X., Zhou, W., Huang, H., 2018a. Bio-oil upgrading by emulsification/microemulsification: a review. *Energy* 161, 214–232.
- Leng, L., Li, J., Wen, Z., Zhou, W., 2018b. Use of microalgae to recycle nutrients in aqueous phase derived from hydrothermal liquefaction process. *Bioresour. Technol.* 256, 529–542.
- Leng, L., Li, J., Yuan, X., Li, J., Han, P., Hong, Y., Wei, F., Zhou, W., 2018c. Beneficial synergistic effect on bio-oil production from co-liquefaction of sewage sludge and lignocellulosic biomass. *Bioresour. Technol.* 251, 49–56.
- Leng, L., Yuan, X., Huang, H., Shao, J., Wang, H., Chen, X., Zeng, G., 2015a. Bio-char derived from sewage sludge by liquefaction: characterization and application for dye adsorption. *Appl. Surf. Sci.* 346, 223–231.
- Leng, L., Yuan, X., Zeng, G., Shao, J., Chen, X., Wu, Z., Wang, H., Peng, X., 2015b. Surface characterization of rice husk bio-char produced by liquefaction and application for cationic dye (Malachite green) adsorption. *Fuel* 155, 77–85.
- Li, F., Cao, X., Zhao, L., Wang, J., Ding, Z., 2014. Effects of mineral additives on biochar formation: carbon retention, stability, and properties. *Environ. Sci. Technol.* 48, 11211–11217.
- Li, H., Wang, S., Yuan, X., Xi, Y., Huang, Z., Tan, M., Li, C., 2018. The effects of temperature and color value on hydrochars' properties in hydrothermal carbonization. *Bioresour. Technol.* 249, 574–581.
- Li, W., Dang, Q., Brown, R.C., Laird, D., Wright, M.M., 2017. The impacts of biomass properties on pyrolysis yields, economic and environmental performance of the pyrolysis-bioenergy-biochar platform to carbon negative energy. *Bioresour. Technol.* 241, 959–968.
- Lian, F., Xing, B., 2017. Black carbon (biochar) in water/soil environments : molecular structure, sorption, stability, and potential risk. *Environ. Sci. Technol.* 51, 13517–13532.
- Liang, B., Lehmann, J., Solomon, D., Sohi, S., Thies, J.E., Skjemstad, J.O., Luizão, F.J., Engelhard, M.H., Neves, E.G., Wirrick, S., 2008. Stability of biomass-derived black carbon in soils. *Geochim. Cosmochim. Acta* 72, 6069–6078.
- Liu, W.J., Jiang, H., Yu, H.Q., 2015. Development of biochar-based functional materials: toward a sustainable platform carbon material. *Chem. Rev.* 115, 12251–12285.
- Liu, X., Zhang, Y., Li, Z., Feng, R., Zhang, Y., 2014. Characterization of corn-cob-derived biochar and pyrolysis kinetics in comparison with corn stalk and sawdust. *Bioresour. Technol.* 170, 76–82.
- Lu, L., Sahajwalla, V., Harris, D., 2000. Characteristics of chars prepared from various pulverized coals at different temperatures using drop-tube furnace. *Energy Fuels* 14, 869–876.
- Manyà, J.J., Azuara, M., Manso, J.A., 2018. Biochar production through slow pyrolysis of different biomass materials: seeking the best operating conditions. *Biomass Bioenergy* 117, 115–123.
- Manyà, J.J., Laguarda, S., Ortigosa, M.A., Manso, J.A., 2014a. Biochar from slow pyrolysis of two-phase olive mill waste: effect of pressure and peak temperature on its potential stability. *Energy Fuels* 28, 3271–3280.
- Manyà, J.J., Ortigosa, M.A., Laguarda, S., Manso, J.A., 2014b. Experimental study on the effect of pyrolysis pressure, peak temperature, and particle size on the potential stability of vine shoots-derived biochar. *Fuel* 133, 163–172.
- Mašek, O., Brownsort, P., Cross, A., Sohi, S., 2013a. Influence of production conditions on the yield and environmental stability of biochar. *Fuel* 103, 151–155.
- Mašek, O., Budarin, V., Gronnow, M., Crombie, K., Brownsort, P., Fitzpatrick, E., Hurst, P., 2013b. Microwave and slow pyrolysis biochar—Comparison of physical and functional properties. *J. Anal. Appl. Pyrol.* 100, 41–48.
- McBeath, A.V., Smernik, R.J., Schneider, M.P.W., Schmidt, M.W.I., Plant, E.L., 2011. Determination of the aromaticity and the degree of aromatic condensation of a thermosequence of wood charcoal using NMR. *Org. Geochem.* 42, 1194–1202.
- McBeath, A.V., Wurster, C.M., Bird, M.I., 2015. Influence of feedstock properties and pyrolysis conditions on biochar carbon stability as determined by hydrogen pyrolysis. *Biomass Bioenergy* 73, 155–173.
- Melligan, F., Aucaisse, R., Novotny, E.H., Leahy, J.J., Hayes, M.H.B., Kwapinski, W., 2011. Pressurized pyrolysis of Miscanthus using a fixed bed reactor. *Bioresour. Technol.* 102, 3466–3470.
- Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* 20, 848–889.
- Morales, V.L., Pérez-Reche, F.J., Hapca, S.M., Hanley, K.L., Lehmann, J., Zhang, W., 2015. Reverse engineering of biochar. *Bioresour. Technol.* 183, 163–174.
- Nguyen, B.T., Lehmann, J., Kinyangi, J., Smernik, R., Riha, S.J., Engelhard, M.H., 2009. Long-term black carbon dynamics in cultivated soil. *Biogeochemistry* 92, 163–176.
- Purakayastha, T.J., Das, K.C., Gaskin, J., Harris, K., Smith, J.L., Kumari, S., 2016. Effect of pyrolysis temperatures on stability and priming effects of C3 and C4 biochars applied to two different soils. *Soil Tillage Res.* 155, 107–115.
- Rafiq, M.K., Joseph, S.D., Li, F., Bai, Y., Shang, Z., Rawal, A., Hook, J.M., Munroe, P.R., Donne, S., Taherymoosavi, S., Mitchell, D.R.G., Pace, B., Mohammed, M., Horvat, J., Marjo, C.E., Wagner, A., Wang, Y., Ye, J., Long, R.J., 2017. Pyrolysis of attapulgite clay blended with yak dung enhances pasture growth and soil health: characterization and initial field trials. *Sci. Total Environ.* 607–608, 184–194.
- Ravishankara, A.R., Daniel, J.S., Portmann, R.W., 2009. Nitrous oxide (N₂O): the dominant ozone-depleting substance emitted in the 21st century. *Science* 80 (326), 123–125.
- Rawal, A., Joseph, S.D., Hook, J.M., Chia, C.H., Munroe, P.R., Donne, S., Lin, Y., Phelan, D., Mitchell, D.R.G., Pace, B., Horvat, J., Webber, J.B.W., 2016. Mineral-biochar composites: molecular structure and porosity. *Environ. Sci. Technol.* 50, 7706–7714.
- Ren, N., Tang, Y., Li, M., 2017. Mineral additive enhanced carbon retention and stabilization in sewage sludge-derived biochar. *Process Saf. Environ. Prot.* 5, 70–78.
- Rombolà, A.G., Fabbri, D., Meredith, W., Snape, C.E., Dieguez-Alonso, A., 2016. Molecular characterization of the thermally labile fraction of biochar by hydro-pyrolysis and pyrolysis-GC/MS. *J. Anal. Appl. Pyrol.* 121, 230–239.
- Sigua, G.C., Novak, J.M., Watts, D.W., Cantrell, K.B., Shumaker, P.D., Szögi, A.A., Johnson, M.G., 2014. Carbon mineralization in two ultisols amended with different sources and particle sizes of pyrolyzed biochar. *Chemosphere* 103, 313–321.
- Singh, B., Fang, Y., Cowie, B.C.C., Thomsen, L., 2014. NEXAFS and XPS characterisation of carbon functional groups of fresh and aged biochars. *Org. Geochem.* 77, 1–10.
- Singh, B.P., Cowie, A.L., Smernik, R.J., 2012a. Biochar carbon stability in a clayey soil as a function of feedstock and pyrolysis temperature. *Environ. Sci. Technol.* 46, 11770–11778.
- Singh, N., Abiven, S., Torn, M.S., Schmidt, M.W.I., 2012b. Fire-derived organic carbon in soil turns over on a centennial scale. *Biogeosciences* 9, 2847–2857.
- Sohi, S.P., Krull, E., Lopez-Capel, E., Bol, R., 2010. A Review of biochar and its use and function in soil. *Adv. Agron.* 47–82.
- Sparrevik, M., Cornelissen, G., Sparrevik, M., Adam, C., Martinsen, V., Cornelissen, G., Cornelissen, G., 2015. Emissions of gases and particles from charcoal/biochar production in rural areas using medium-sized traditional and improved “retort” kilns. *Biomass Bioenergy* 72, 65–73.
- Spokas, K., 2010. Review of the stability of biochar in soils: predictability of O: C molar ratios. *Carbon Manage.* 1, 289–303.
- Suárez-Abelenda, M., Kaal, J., McBeath, A.V., 2017. Translating analytical pyrolysis fingerprints to Thermal Stability Indices (TSI) to improve biochar characterization by pyrolysis-GC-MS. *Biomass Bioenergy* 98, 306–320.
- Sun, H., Hockaday, W.C., Masiello, C.A., Zygourakis, K., 2012. Multiple controls on the chemical and physical structure of biochars. *Ind. Eng. Chem. Res.* 51, 3587–3597.
- Tan, X., Liu, Y., Gu, Y., Xu, Y., Zeng, G., Hu, X., Liu, S., Wang, X., Liu, S., Li, J., 2016. Biochar-based nano-composites for the decontamination of wastewater: a review. *Bioresour. Technol.* 212, 318–333.
- Tan, X., Liu, S., Liu, Y., Gu, Y., Zeng, G., Hu, X., Wang, X., Liu, S., Jiang, L., 2017. Biochar as potential sustainable precursors for activated carbon production: multiple applications in environmental protection and energy storage. *Bioresour. Technol.* 227, 359–372.
- Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* 125, 70–85.
- Tripathi, M., Sahu, J.N., Ganesan, P., 2016. Effect of process parameters on production of biochar from biomass waste through pyrolysis: a review. *Renew. Sustain. Energy Rev.* 55, 467–481.
- Wang, J., Xiong, Z., Kuzyakov, Y., 2016. Biochar stability in soil: meta-analysis of decomposition and priming effects. *GCB Bioenergy* 8, 512–523.
- Wang, S., Dai, G., Yang, H., Luo, Z., 2017. Lignocellulosic biomass pyrolysis mechanism: a state-of-the-art review. *Prog. Energy Combust. Sci.* 62, 33–86.
- Wang, Y., Jiang, L., Dai, L., Yu, Z., Liu, Y., Ruan, R., Fu, G., Zhou, Y., Fan, L., Duan, D., Zhao, Y., 2018. Microwave-assisted catalytic co-pyrolysis of soybean straw and soapstock for bio-oil production using SiC ceramic foam catalyst. *J. Anal. Appl. Pyrol.* 133, 76–81.
- Weber, K., Quicker, P., 2018. Properties of biochar. *Fuel* 217, 240–261.
- Wiedemeier, D.B., Abiven, S., Hockaday, W.C., Keilueit, M., Kleber, M., Masiello, C.A., McBeath, A.V., Nico, P.S., Pyle, L.A., Schneider, M.P.W., Smernik, R.J., Wiesenberger, G.L.B., Schmidt, M.W.I., 2015a. Aromaticity and degree of aromatic condensation of char. *Org. Geochem.* 78, 135–143.
- Wiedemeier, D.B., Brodowski, S., Wiesenberger, G.L.B., 2015b. Pyrogenic molecular markers: linking PAH with BPCA analysis. *Chemosphere* 119, 432–437.
- Wilson, F., Tremain, P., Moghtaderi, B., 2018. Characterization of biochars derived from pyrolysis of biomass and calcium oxide mixtures. *Energy Fuels* 32, 4167–4177.
- Windeatt, J.H., Ross, A.B., Williams, P.T., Forster, P.M., Nahil, M.A., Singh, S., 2014. Characteristics of biochars from crop residues: potential for carbon sequestration and soil amendment. *J. Environ. Manage.* 146, 189–197.
- Wu, W., Yang, M., Feng, Q., McGrouther, K., Wang, H., Lu, H., Chen, Y., 2012. Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass Bioenergy* 47, 268–276.
- Xiao, R., Wang, J.J., Gaston, L.A., Zhou, B., Park, J., Li, R., Dodla, S.K., Zhang, Z., 2018. Biochar produced from mineral salt-impregnated chicken manure : fertility properties and potential for carbon sequestration. *Waste Manage.* 78, 802–810.
- Xu, X., Hu, X., Ding, Z., Chen, Y., 2017a. Effects of copyrolysis of sludge with calcium carbonate and calcium hydrogen phosphate on chemical stability of carbon and release of toxic elements in the resultant biochars. *Chemosphere* 189, 76–85.
- Xu, X., Zhao, Y., Sima, J., Zhao, L., Mašek, O., Cao, X., 2017b. Indispensable role of biochar-inherent mineral constituents in its environmental applications: a review. *Bioresour. Technol.* 241, 887–899.
- Yang, F., Xu, Z., Yu, L., Gao, B., Xu, X., Zhao, L., Cao, X., 2018a. Kaolinite enhances the stability of the dissolvable and undissolvable fractions of biochar via different mechanisms. *Environ. Sci. Technol.* 52, 8321–8329.
- Yang, F., Zhao, L., Gao, B., Xu, X., Cao, X., 2016. The Interfacial behavior between biochar and soil minerals and its effect on biochar stability. *Environ. Sci. Technol.* 50, 2264–2271.
- Yang, Y., Sun, K., Han, L., Jin, J., Sun, H., Yang, Y., Xing, B., 2018b. Effect of minerals on the stability of biochar. *Chemosphere* 204, 310–317.

- Zhang, J., Liu, J., Liu, R., 2015. Effects of pyrolysis temperature and heating time on biochar obtained from the pyrolysis of straw and lignosulfonate. *Bioresour. Technol.* 176, 288–291.
- Zhao, L., Cao, X., Mašek, O., Zimmerman, A., 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. *J. Hazard. Mater.* 256–257, 1–9.
- Zimmerman, A.R., 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environ. Sci. Technol.* 44, 1295–1301.
- Zimmerman, A.R., Gao, B., Ahn, M.Y., 2011. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biol. Biochem.* 43, 1169–1179.
- Zornoza, R., Moreno-Barriga, F., Acosta, J.A., Muñoz, M.A., Faz, A., 2016. Stability, nutrient availability and hydrophobicity of biochars derived from manure, crop residues, and municipal solid waste for their use as soil amendments. *Chemosphere* 144, 122–130.